Synthesis and Characterization of Biobased Lactose Hydrogels: A Teaching Experiment on Sustainable Polymers and Waste Biomass Valorization

Jeffrey Paz Buenaflor[†], Marc A. Hillmyer[†], Michael T. Wentzel[&], and Jane E. Wissinger*[†]

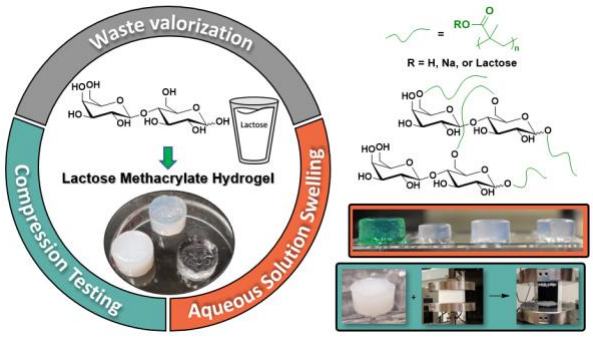
[†]Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

[&]Department of Chemistry, Augsburg University, Minneapolis, Minnesota 55454

ABSTRACT

Hydrogels are soft water-rich materials with physical properties that are easily tuned by modifying their network structure. For instance, increasing or decreasing the crosslinking density has a profound effect on their water absorption capabilities and mechanical strength. These physical changes are showcased in a new experiment for organic chemistry and polymer science teaching laboratories based on a practical green synthesis and characterization of lactose methacrylate derived hydrogels. Lactose, a disaccharide derived from dairy waste byproducts, is functionalized with photoreactive methacrylate groups using methacrylic anhydride. The resulting mixture is subsequently photoirradiated to generate a crosslinked hydrogel. Structure-property relationships are assessed through comparative studies of three hydrogels of varying compositions. Compression tests and swelling studies in different aqueous environments offer a guided-inquiry experience. Students determine a relationship between crosslinking density and the physical properties of the hydrogels. This experiment highlights the valorization of biomass and multiple green chemistry principles including use of renewable feedstocks, atom economy, energy efficiency, waste prevention and water as a benign solvent. Learning outcomes for an organic chemistry laboratory course include introduction to disaccharide and crosslinked polymer structures, observable physical change dependency with crosslinking density, and laboratory methods for evaluating water absorption capacities. Objectives aligned with a polymer course are incorporating mechanical compression instrumentation, mechanistic understanding of light-induced free radical polymerizations and an appreciation for the application of hydrogels to commercial products. Overall, the translation of a current literature publication to an inexpensive and versatile experiment engages students in a modern example of sustainable polymer chemistry.

GRAPHICAL ABSTRACT



KEYWORDS

Second-Year Undergraduate, Upper-Division Undergraduate, Laboratory Instruction, Organic Chemistry, Polymer Chemistry, Hands-On Learning, Inquiry-Based, Carbohydrates, Green Chemistry, Materials Science, Polymerization

INTRODUCTION

Hydrogels are crosslinked networks that can be comprised of synthetic polymers[1], biopolymers[2], or a hybrid combination.[3] They are designed to absorb and retain large amounts of water several times greater than their original dried mass. A polymeric hydrogel network can be comprised of covalent, electrostatic, or physical crosslinks. Development of hydrogels with stimuli-responsive, dynamic, or tunable mechanical properties make them highly desirable in biomedical applications such as tissue engineering, drug delivery, wound bandaging, and hygienic consumer products.[4]

Lactose (1) is a naturally occurring disaccharide comprised of a galactose and glucose unit covalently linked through a β-(1,4)-glycosidic linkage. This carbohydrate can be sourced from whey, the liquid remnant after milk is coagulated and a byproduct of the dairy industry. The composition of whey is mostly water and total solids at approximately 6.5% of its mass.[5] Of the total solids, lactose represents about 75% while proteins and minerals make up the balance. In 2021, an estimated 3 billion pounds of dairy products in the form of dry milk powders and whey products were produced annually in the United States.[6] In 2020, the estimated global production of whey was 168 million tons and about 50% was treated as waste or used as animal feed or fertilizer.[7] The amount of unused whey represents an opportunity for valorization of dairy waste to generate hydrophilic materials, such as hydrogels, since the lactose framework contains multiple hydroxyl functionalities.

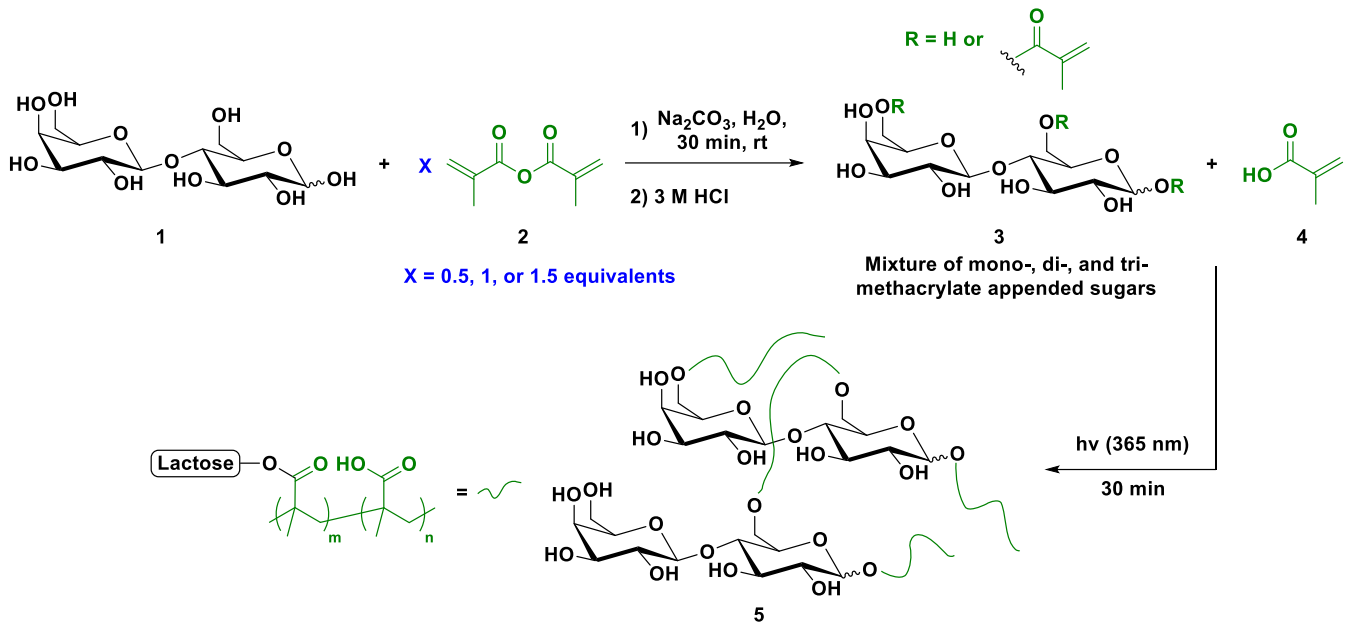
Valorization of biomass involves the transformation of renewable, waste, or recycled feedstocks to value added materials for the synthesis of new polymers.[8] This addresses a major tenet of the Sustainable Polymer Framework[9] in which petroleum-derived feedstocks are replaced with waste as

raw materials. In terms of sustainability and green chemistry, valorization of biomass has the potential benefit of reducing our carbon footprint as well.

Examples of waste valorization exist in the education literature and include the extraction of tannins from acorns[10], the exploration of humin byproducts from the acid-catalyzed reactions involving sugars sourced from lignocelluloses[11], conversion of pineapple waste to biofuels[12], generation of adsorbents from fruit and vegetable peels[13], and others.[14,15] For teaching purposes, the tunable properties of hydrogels provide varied opportunities for engagement of students from K-12 to upper level undergraduates depending on the desired application.[3,16–19]

Herein, we describe the design of a partially biobased hydrogel teaching experiment that highlights the valorization of lactose from dairy waste and green chemistry principles. The experiment is a translation of published research[20] by the NSF Center for Sustainable Polymers into a safe and inexpensive teaching activity.[21] A two-step atom-economical reaction modifies lactose with methyl methacrylate groups that are subsequently crosslinked using free-radical polymerization under UV light (Scheme 1). Iterative implementations in an organic chemistry laboratory course and three semesters of an upper division polymer course were used to optimize the experimental protocols. For the organic chemistry course, students were introduced to the carbohydrate structure of lactose and esterification of hydroxyl groups using an anhydride; a reaction commonly taught in organic chemistry lecture courses. The experimental procedure focused on students' observations of hydrogel appearance related to crosslinking density and evaluation of swelling properties in solutions of varying pH. Assignments probed their understanding of structure-property relationships of the hydrogels. Students in the polymer course completed an upper division polymer lecture course and thus learning outcomes were expanded to include mechanisms of free-radical polymerizations and compression testing for the determination of Young's modulus. Overall, student assessments demonstrated a high success rate both at the bench and toward learning outcomes.

Scheme 1. Two-step synthesis of lactose methacrylate hydrogels of varying crosslinking densities



Two-step Synthesis of Lactose Methacrylate Hydrogels

Lactose (1) is esterified through the nucleophilic addition of hydroxyl groups to varying equivalents of methacrylic anhydride (2). The elimination of the methacrylate anion under basic conditions drives the reaction towards a product mixture containing mono-, di-, and trimethacrylated sugars (3) and the byproduct sodium methacrylate. Neutralization of the mixture with acid produces methacrylic acid (4) which then serves as a co-monomer in the subsequent reaction. Per the original publication,[20] the anomeric and primary alcohols are presumed most reactive; however, efforts to determine the precise composition of this mixture were unsuccessful using a variety of analytical tools including electrospray ionization mass spectrometry, ^{1}H NMR spectroscopy and various chromatographic analytical tools. The reaction mixture (3 + 4) is subsequently photoirradiated at 365 nm to generate the crosslinked hydrogel (5). Rheological data showed a correlation of increased crosslinking density with increasing ratios of methacrylic anhydride used to form the derivatized lactose.[20] Several features of the synthesis of the lactose hydrogels align with the 12 Principles of Green Chemistry[22]:

- Atom economy (#2) and generation of minimal waste (#1)
- Use of renewable/waste feedstocks (#7) and a benign solvent (water) (#5)
- Energy efficient (#6) synthesis conducted at ambient temperature and short reaction times

As mentioned above, methacrylic acid (4) is the byproduct in the first synthetic step and serves as a comonomer during the subsequent crosslinking. In contrast to most nucleophilic substitution

reactions where leaving groups are discarded as waste, in this synthesis, the byproduct is used as a reactant and is incorporated into the final product. Another green feature lies in the photopolymerization step that does not require an exogenous photoinitiator. Methacrylates are known for their ability to self-initiate under irradiation.[23,24] The facile chemistry to access lactose-containing polymers in this experiment makes it ideal for a teaching laboratory setting. Previous works on lactose-containing polymers typically involved multi-step syntheses and the need for protecting groups.[25–29]

Hydrogel Water Swelling and Mechanical Behavior

The synthesized materials exhibit water absorption and mechanical properties suitable for incorporation into a teaching laboratory experiment. Polymer concepts such as the relationship between material properties and crosslinking density can be studied. For example, water uptake capacities are affected by the pH and ionic strength of the swelling medium.[30,31] The lactose methacrylate hydrogels (5) possess varying amounts of carboxylate groups that are incorporated through the methacrylic acid co-monomer. Depending on the pH, the carboxylate groups exist in a neutral or negatively charged state, which in turn impacts the affinity of the hydrogel product for water. Lactose methacrylate hydrogels with varying crosslinking density were easily compared by testing their swelling capabilities. Students evaluated the swelling behavior by taking into account how water uptake was affected by the intermolecular, osmotic, and hydration forces.[32]

For compression tests, the mechanical behavior that hydrogels exhibit during deformation are affected by the amount of crosslinking in the network.[33] The compression rigidity (modulus) and extensibility are largely dependent on the covalent crosslinking content. Brittle hydrogels typically have high chemical crosslink density and exhibit low deformation before fracturing at relatively low strains. Hydrogels with lower crosslink density are softer and somewhat more flexible. They can be elongated to higher strains before fracturing. The lactose methacrylate hydrogels exhibit these trends and students observe the effects studying the different crosslinking densities by measuring compressive modulus and failure strain.

EXPERIMENTAL SECTION

Materials and Instrumentation

Reagents were purchased from commercial suppliers (Sigma-Aldrich, Fisher Scientific, VWR International) and unless noted, were used as received without further purification. All 50 mM buffer (citric acid, phosphate, and carbonate/bicarbonate) solutions used in swelling tests were freshly prepared the day of the laboratory course experiment.

Lactose derivatives (3) were synthesized in 20 mL scintillation vials stirred at room temperature. Polymer formation was conducted in Falcon® 24-well plates[34] placed inside the chamber of a 365 nm MelodySusie 36W Nail Lamp[35].. The polymeric products were transported on watch glasses or aluminum plates.

Swelling tests were completed in either beakers covered with parafilm or specimen cups. Collection of swelled hydrogels and filtration of buffer solutions involved Biologix 15-1040-1 polyethylene cell strainers with 40-micron mesh.

Stress-strain data under compression was obtained on an Instron 3342 instrument with two parallel stainless-steel platens at a uniaxial compression rate of 1 mm/min on cylindrical hydrogel samples. Students followed instructions to operate the Instron instrument. Once the mechanical tests were completed, students received a file containing the displacement (*x*-values) and force (*y*-values) raw data and then converted them to strain % and stress values, respectively.

Experiment Overview

The experiment was performed in consecutive laboratory periods a week apart. The first lab period, taking at least 3 hours, but no more than the 3 h and 50 min lab period, included synthesis of the hydrogels, preparation of swelling baths, and compression testing (for the polymer course). The two-step synthesis of the hydrogel, including preparation and work up, can be completed in 1.5–2 h. During each step of the synthesis, there is time for preparing the pH swelling solutions and familiarization with the compression instrument. Typically, six cylindrical hydrogels were created per reaction condition. Four of the hydrogels were placed in their pH baths and swelled for one week until the next lab period. One hydrogel was used for the compression testing. The sixth was washed in a DI H_2O bath for a minimum of 15 min and allowed to dry on an aluminum weigh boat until the next lab period. The second lab period required 1–1.5 h and focused on analyzing the swelling of the hydrogels.

An optional comparison test between a commercially available water adsorbent and the dried hydrogel can be conducted where both materials were swelled for 10 min and their masses were measured.

Hydrogel Synthesis

Three hydrogels varying in crosslinking density were assigned overall to the class (Table 1). Student groups explored two different reactant stoichiometries, producing two sets of six hydrogels per composition. Specific details are found in the Supporting Information (SI). Lactose monohydrate was dissolved in DI water at 65 °C in a 20 mL scintillation vial on an aluminum heating block (Figure 1a) and then cooled to room temperature. Methacrylic anhydride and sodium carbonate were subsequently added to the vial resulting in an immiscible mixture that was stirred vigorously at room temperature for at least 30 min and up to 60 min. Vigorous stirring (400-450 rpm) ensured the required interface between the immiscible methacrylic anhydride and the lactose in the aqueous phase for efficient reaction and consistently high-quality hydrogels. On a few occasions when student groups did not adhere to the stirring instructions, lower quality hydrogels with weaker mechanical properties formed. After the reaction was complete, the mixture was neutralized by the dropwise addition of 3.0 M HCl. It was essential that the solution was stirred during neutralization and that the pH was monitored by litmus paper. After neutralization, the reaction mixture was distributed between six wells of a Falcon® 24-well plate (Figure 1b). The well plates were inserted into a MelodySusie UV Lamp to be crosslinked via photoirradiation for 30 min (Figure 1c). The cured hydrogels were removed from the individual wells and observations were made regarding their appearance and apparent mechanical strength (Figure 1d and e).

Table 1. Reaction conditions used to prepare three different hydrogels of varying crosslinking densities

Condition[a]	*Lactose : MAH : Base*	*Lactose (g)*	*MAH (mL)*	*Na_2CO_3 (g)*
A	1 : 0.5 : 0.25	5	1	0.368
B	1 : 1.0 : 0.50	5	2	0.735
C	1 : 1.5 : 0.75	5	3	1.103

[a]All reactions were carried out in 10 mL of DI H_2O at ambient temperature

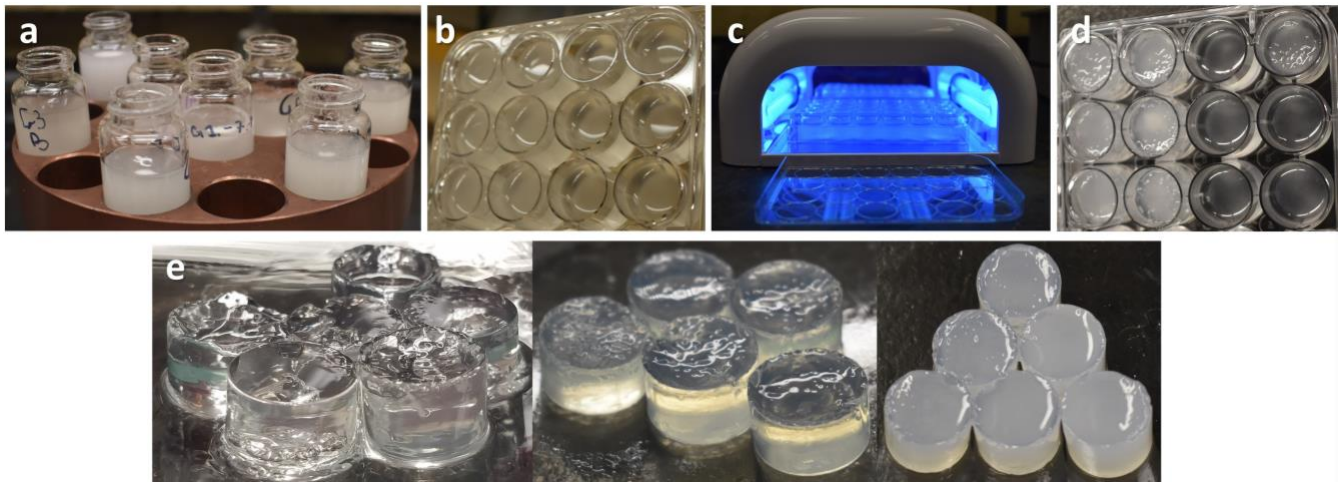


Figure 1. Steps of the hydrogel synthesis: a) Alcoholysis of methacrylic anhydride with lactose; b) Well-plates containing polymer precursor mixture; c) Photoirradiation under the MelodySusie lamp; d) Photopolymerized hydrogels; e) Three hydrogels with increasing crosslinking density from left to right and observable trend from transparent to translucent to opaque in appearance.

pH Swelling Tests

Groups recorded the mass of four hydrogels of the same composition before each was placed in a different aqueous environment. Solutions containing citric acid, phosphates, carbonate/bicarbonate, and deionized H_2O (optionally colored with a food dye for aesthetics) were studied. The swelling tests can be conducted in Parafilm covered beakers or capped specimen cups (Figure 2a & 2b). The hydrogels were left in the swelling baths for one week and their new masses were recorded during the next lab period (Figure 2c). To collect the swelled hydrogels, the aqueous solution was carefully poured through a strainer (to maintain the integrity of hydrogel shape) into an Erlenmeyer flask (Figure 2d). After removing excess aqueous solution on the hydrogel surface with a Kimwipe™, the mass of the swelled hydrogel was recorded. The amount of water absorbed by each hydrogel was calculated using Eq. 1 where m_1 is the mass before swelling and m_2 is the mass after swelling. Note that Eq. 1 determines comparative water uptake and not an absolute value. If total water content is desired, the initial water content of each sample A, B, and C, could be determined by measuring the mass of a dried sample.

$$Change\ in\ water\ content\ \% = \left(\frac{m_2 - m_1}{m_1}\right) \times 100\% \quad (1)$$

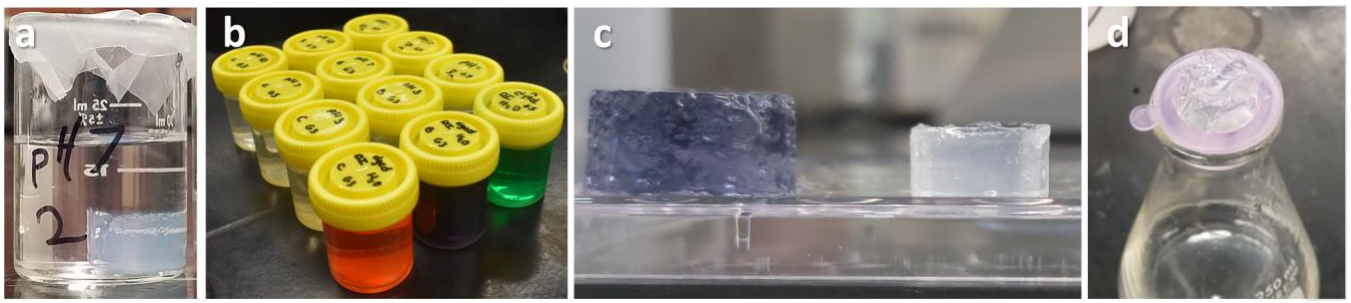


Figure 2. a) Parafilm covered beaker swelling test; b) capped specimen swelling tests; c) Examples of swelled hydrogels; d) Collection of hydrogels using strainer.

The remaining sixth hydrogel was soaked in a DI H_2O bath to remove salts and unreacted starting material. Before the end of the first lab period, students removed the hydrogels and placed them on an aluminum dish to dry over one week before the second lab period. The dried hydrogel was used in the second laboratory period for an optional swelling test involving a comparison with sodium polyacrylate. After grinding the solid into a granular material, 20 mg of material was placed into a beaker and swelled in DI H_2O for 10 min. The same process was repeated with 20 mg of sodium polyacrylate that was obtained from a commercially available diaper. Observations and swelled masses were recorded (see SI for details).

Compression Testing

Each group evaluated the stress-strain characteristics of one hydrogel per set using the Instron 3342 instrument instructions to measure the compressive modulus. The diameter and thickness (in mm) of the cylindrical hydrogel was measured and inputted into the Instron software. The hydrogel was placed in the middle of the lower platen situated atop of a small piece filter paper (Figure 3a). This safety precaution prevented the hydrogel from slipping and accidentally being ejected from the instrument. Once ready, the upper platen was lowered to the very top of the hydrogel and the test was initiated. Hydrogels were uniaxially compressed at a send speed of 1 mm/min. While the instrument was running, vibrations and disturbances on the instrument table were minimized to prevent inaccuracies in the recording of data. The run was complete once catastrophic failure was reached (Figure 3b & c). This was commensurate with a precipitous reduction in the stress at the failure strain. The stress-strain curve was obtained by converting the raw data containing displacement (mm) and force (kN) into strain % and stress (kPa), respectively. Strain % was calculated by dividing

displacement (Δl) by the thickness (l_o) of the hydrogel (Eq. 2) and multiplying by 100%. Stress was calculated by dividing the measured force by the circular cross-sectional area of the cylindrical disc (Eq. 3). Students were instructed to be mindful of dimensional analysis, particularly when calculating stress, since one Pascal (Pa) is one Newton (N) per meter (m) squared. Compressive modulus (E) was determined in the region where strain was sufficiently small such that stress remained linearly proportional to strain. The slope of this region, typically at the beginning of the curve at the lowest strains under compressive stress, was used to calculate compressive modulus. To ascertain this region, one must ensure a stress was recorded; otherwise, the modulus value is unreliable.

$$\% \, Strain = -\left(\frac{\Delta l}{l}\right) \times 100\% \tag{2}$$

$$Stress = \left(\frac{F}{\pi r^2}\right) \tag{3}$$

Figure 3. Steps of the compression tests: a) Hydrogel placed on filter paper before compression; b) Ongoing compression testing of hydrogel; c) Appearance of hydrogel after compression

HAZARDS

Methacrylic anhydride and the byproduct methacrylic acid are combustible liquids, corrosive, and irritants. Both chemicals have a detectable odor and should always be handled in a fume hood with gloves. Sodium carbonate and sodium methacrylate, another byproduct of the reaction, are known irritants. Lactose monohydrate is classified as a non-hazardous substance. pH swelling solutions containing citric acid and sodium carbonate/bicarbonate are corrosive and gloves should be worn when recovering the hydrogels.

RESULTS AND DISCUSSION

Classroom Implementation

Four successful implementations of the experiment were conducted in laboratory courses from a first semester organic chemistry lab at Augsburg University (AU, fall 2021), a small university, and an advanced polymer lab at the University of Minnesota (UMN, spring 2021-2023), a large university.

Students either worked alone, in pairs, or in groups of three, depending on the class size. Since these implementations occurred during the ongoing COVID-19 pandemic, average class sizes were smaller than typical, and adjustments were made to obtain more data by having students synthesize two sets of hydrogels of different compositions. At Augsburg University, students were from a variety of majors typical of a first semester organic chemistry course. The advanced polymer lab consisted of upper division students in the chemistry, chemical engineering, and materials sciences undergraduate programs.

Course materials and assignments were tailored appropriately regarding the level of lab experience. For both laboratory courses, a 25 min lecture covered the lab objectives and topics that introduced the concepts of hydrogels, green chemistry, and sustainability. Structure-property relationships focusing on the effect of crosslinking on hydrogel physical behavior were emphasized to engage students in a guided-inquiry study. This exposed students to several principles of green chemistry, strategies to design sustainable polymers, and methods of assessing material properties. The swelling tests were performed in both the organic chemistry and polymer courses, whereas compression was also incorporated into the UMN polymer curriculum. The data collected by students were shared in a class Google spreadsheet so that comparisons could be drawn between all hydrogels prepared by the class and used to address questions on assigned worksheets and laboratory reports.

pH Swelling Tests

The comparisons of water swellings in different aqueous media are illustrated in Figure 4 and Table 2 (See Tables S7 and S8 from SI). In addition to the effect of crosslinking on water absorption, students examined aqueous environments differing in pH and ionic strength. As expected, when examining the effect of crosslinking density, students observed that the higher the initial methacrylic anhydride concentration, the lower the water uptake capabilities of the hydrogel. This can be attributed to the tighter crosslinked network of the hydrogel.[36] The reduced space between network junctions decreases the amount of water that the hydrogel can uptake.

When analyzing pH, water absorption was drastically reduced in pH 3 media and in several cases, students reported loss of water content in the hydrogel. This can be attributed to the pH being lower than the pKa of the poly(methacrylic acid) (PMAA) chains, which is approximately between 5-6.[37,38] At pH 3, the carboxyl groups on the PMAA portion of the hydrogel are protonated leading to a neutral

structure that is much less hydrophilic as compared to the carboxylate anions. Additionally, the reduction in both degree of ionization and electrostatic repulsion of the negatively-charged carboxyl groups on the polymer chains leads to the collapse of the hydrogel network shrinking its size.[32,39] At a pH greater than the pKa of PMAA, the carboxyl groups are ionized and much more hydrophilic. The electrostatic repulsion inside the network expands the pores of the hydrogel network and increases swelling. Hydrogels swell more in higher pH, with swelling ratios being slightly larger at pH 10. Hydrogels containing ionized carboxylic acid groups submerged in DI H_2O exhibit the greatest amount of swelling. In this environment, the charge screening effect is diminished since there are insufficient ions present to shield the carboxylate groups from intermolecular repulsions. The lack of ions in DI H_2O and the increased osmotic drive to swell the hydrogel, led to observed higher swelling ratios.

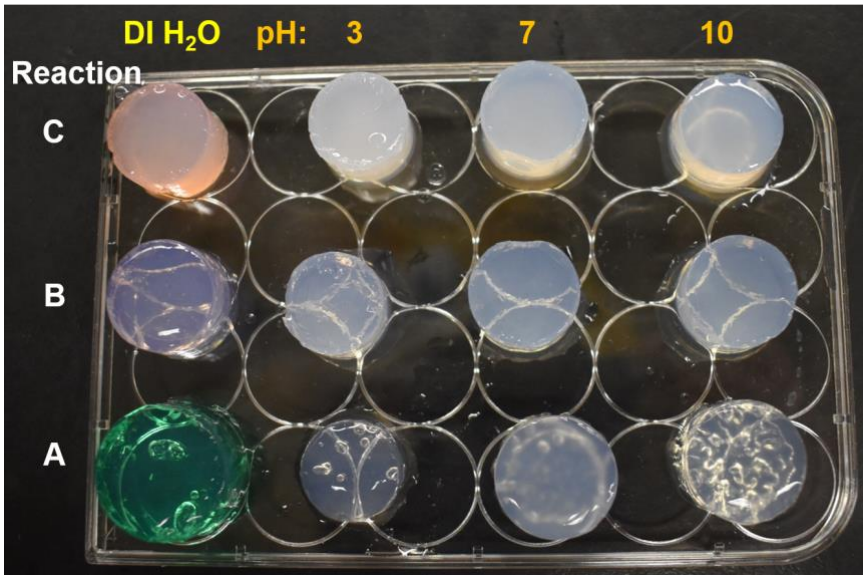


Figure 4. Comparison of swelled hydrogels in varying aqueous environments illustrating the trend from transparent to translucent to opaque with increasing crosslinking density from A to C. Food dye was added to the DI H_2O tests for visibility and aesthetics.

Table 2. Student swelling data (Spring 2023)

Reaction	***Lac:MAH***	***% Water uptake***			
		pH 3	*pH 7*	*pH 10*	*DI H_2O*
A	1:0.5	14 ± 14	44 ± 15	93 ± 37	226 ± 34
B	1:1.0	23 ± 7	29 ± 2	51 ± 15	68 ± 4
C	1:1.5	9 ± 8	19 ± 2	24 ± 12	39 ± 14

Compression Testing Results

Before the compression tests, groups assessed the relative mechanical strength of the three different hydrogel compositions by examining their samples and neighboring group's materials for

firmness. Predictions were made on the expected trends associated with changing the crosslinking density of the hydrogel network. Stress-strain curves were generated from displacement and force data extracted from the compression tests. This data was used to determine Young's compressive modulus and failure strain (Table 3). Failure strain was determined at the point where the stress is released (drops downward on the curve) due the fracturing of the hydrogel. Figure 5 and Figure S4 in the SI illustrate representative curves of student data. These compared favorably to research data depicted in Figures S5 and S6 in the SI.

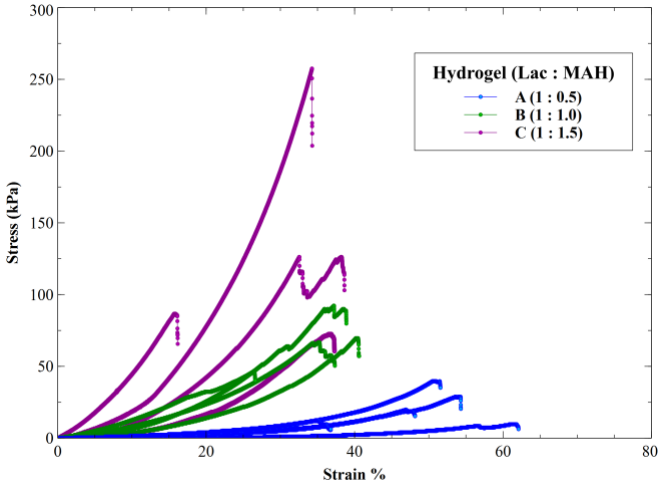


Figure 5. Spring 2023 student group stress-strain curves of three different hydrogels

Table 3. Student modulus and strain data (Spring 2023)

Reaction	*Lac : MAH*	*E* (kPa)[a]	*Failure Strain %*
A	1 : 0.5	15 ± 7	52 ± 10
B	1 : 1.0	100 ± 30	36 ± 6
C	1 : 1.5	265 ± 165	32 ± 11

[a]*Modulus (E) was determined by the slope of initial linear region of the stress strain data*

As mentioned previously for elastic materials, stress and strain are directly proportional at small enough values of strain. This relationship was used to obtain compressive modulus by determining the slope. Calculating compressive modulus at small strain values was relatively easy for hydrogels B and C, which immediately exhibited significant stress. This was not the case for hydrogels A, where significant portions of the early % strain region did not give measurable values for stress using the instrument. We attributed this issue to the inherent softness of hydrogels prepared under Reaction A

conditions. While there was apparent strain as the hydrogel deformed with the platen pressing down, the compression instrument, with force transducer limits from -105 to 105 newtons, displayed measurable stress at regions typically beyond 10-20% strain. Students were tasked with determining compressive modulus for the hydrogels using these low % strain regions.

In the three implementations at UMN where compressive studies were conducted, students were mostly successful in producing stress-strain curves that exhibited expected trends for hydrogels synthesized with varying crosslinking densities. Students observed that crosslinking density has a direct relationship with modulus and inverse relationship with strain at failure. Hydrogels constructed with a higher concentration of methyl methacrylate chemical crosslinks were brittle, exhibited lower strain failure values, and required high stress to fracture. Hydrogels synthesized with the lowest concentration of chemical crosslinks were flexible, somewhat elastic, and possessed the lowest modulus values.

Hydrogel C generally requires high stress to fracture. Spring 2023 data for hydrogel C exhibited the widest variation and deviation of expected mechanical properties due to non-uniformity of the hydrogels. An example of a non-uniform hydrogel is displayed in Figure S9a in the SI. Non-uniform hydrogels result from poor mixing in the first step or through CO_2 bubbles produced during the acidic workup. Hydrogels with irregular shapes and bubbles (that can be considered defects in the material to facilitate premature fracture) fragment easily at lower stress due to the weakened hydrogel structure.

Assessment of Learning Objectives and Student Feedback

Student understanding of the experiment's learning objectives was assessed through an assignment sheet or full laboratory report. Student experimental data and feedback were collected via a Google form survey and determined to be exempt of IRB review (U of MN, IRB ID: STUDY00011272). Figures 6 and 7 are results from the assignment and student survey of the UMN Polymer laboratory course, spring 2022 and spring 2023. (See SI for full survey).

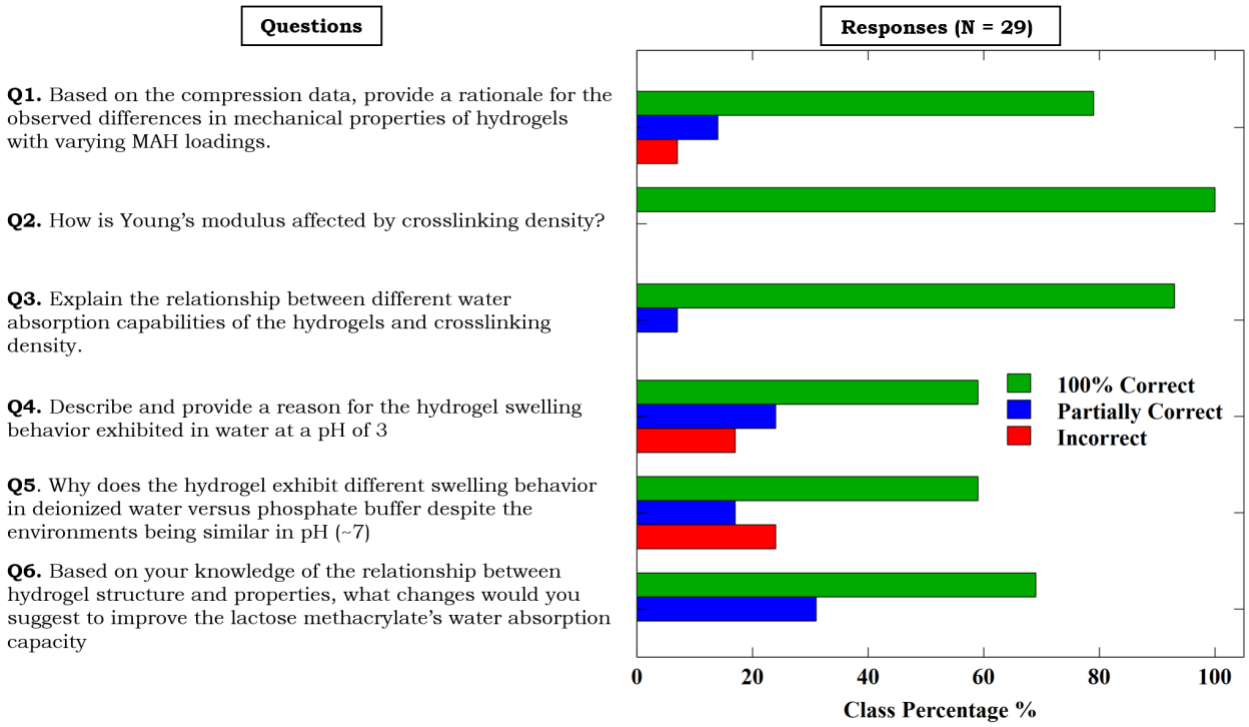


Figure 6. Assessment of student understanding of hydrogel structure-property relationships through graded free response assignment collected spring 2022 and spring 2023

Overall, students performed well in the assignment providing primarily correct responses in the interpretation of the data and demonstrated understanding of the mechanisms behind the hydrogel physical properties (class average: 84%). When analyzing the content related to mechanical behavior, students had a solid grasp on how crosslinking affects the strength and extensibility of the hydrogels. They understood the direct relationship between modulus and crosslinking. Interestingly, when it came to surveying their interpretation of modulus and stress-strain curves, this statement received the lowest score and highest standard deviation. Throughout discussions with students, the most challenging aspect involved properly identifying the initial linear region of the stress strain data, which was needed to calculate the compressive modulus. This was primarily the case for hydrogel A as discussed previously, which caused the most confusion for students.

While the number of correct responses for analyzing swelling properties were lower compared to the mechanical properties of hydrogels, overall students demonstrated knowledge of the concepts. The impact of crosslinking on hydrogel water absorption was correctly identified by students. Most students generally understood that multiple factors can affect hydrogel swelling as was illustrated with

the different pH swelling tests. When asked how to improve the water swelling capabilities of the lactose methacrylate hydrogels, students were able to provide singular or multiple changes based on their understanding of polymer structure and electrostatic interactions.

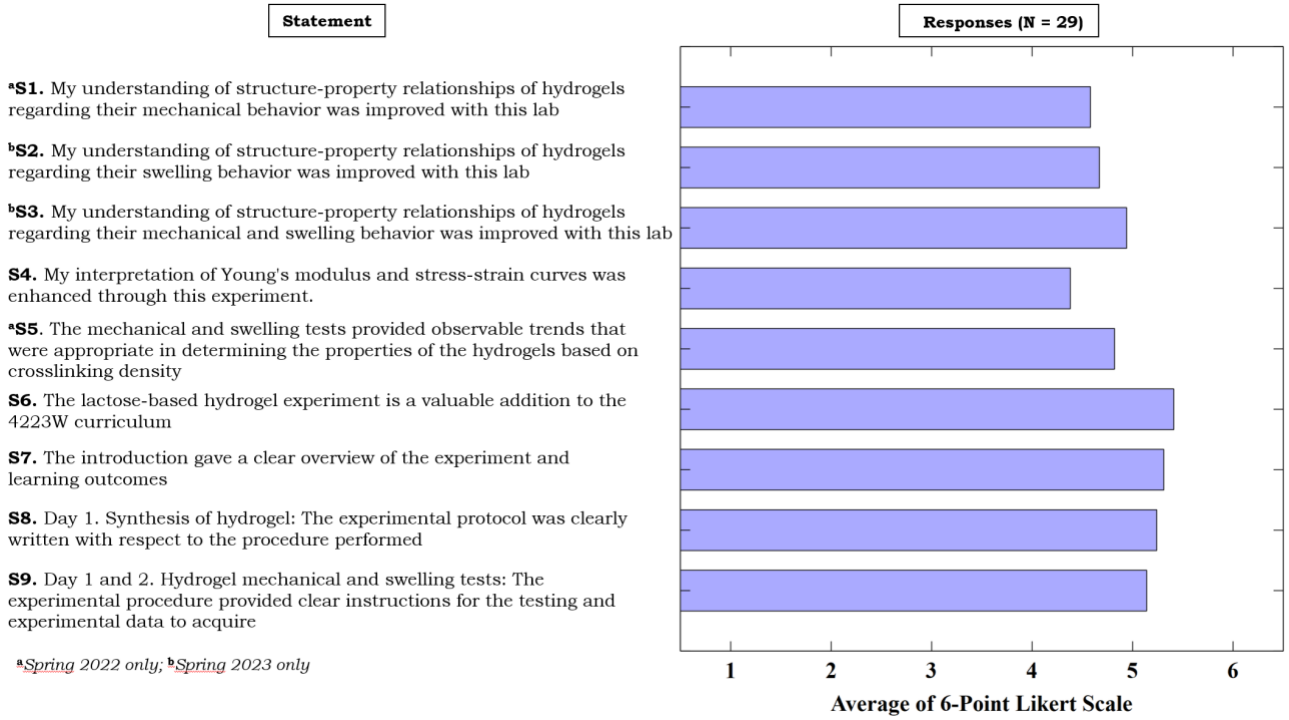


Figure 7. Student evaluation of the experiment via Google form survey (UMN Advanced Polymer Course 2022 and 2023). A Likert Scale was used with 1 = strongly disagree, 2 = disagree, 3 = slightly disagree, 4 = slightly agree, 5 = agree, 6 = strongly agree.

The learning objectives and the quantification of polymer properties in this experiment were successfully achieved as shown by the student feedback. The expected trends in both mechanical and swelling behavior were observed and 76% of the class agreed or strongly agreed that the observable trends could be used to determine the hydrogel properties. Student perception in the survey reflected an improved understanding of structure-property relationships as 79% of the students agreed or strongly agreed with this statement. This experiment exposed students to concepts outside of chemistry that are typically seen in materials science.

A summary of additional survey questions, as found in the SI, indicated that 86% of the students agreed or strongly agreed that it was a “valuable addition” to the polymer laboratory course. When given a list of options, the three aspects of the experiment students appreciated the most were:

- Comparing swelling properties of synthesized hydrogels to a commercially available product

- Performing a synthesis that exemplifies a high degree of green chemistry principles
- Synthesizing a material and exploring its tunable swelling and mechanical properties

Lastly, when prompted to provide any further comments, impressions left by the students were overwhelmingly positive:

- I really enjoyed this lab. The results were tangible with comprehensive analysis that connected directly to science I've seen in journals
- I enjoy labs like this that are creative. Please continue to encourage creativity in this lab and others.
- Lab 7 was extremely enjoyable and different than other labs performed this semester

CONCLUSION

We report a polymer teaching experiment that incorporates green and sustainable chemistry principles and illustrates the potential valorization of a material sourced from dairy waste into a hydrogel. The reactants are readily available and inexpensive leading to a cost of approximately $1 per student. The experiment is straightforward and accessible to both introductory organic and upper division polymer laboratory courses. The easily modifiable properties of the hydrogels provided an appropriate number of parameters to explore in a teaching setting.

As with every new experiment, there is opportunity for modifications, extensions, and improvements. For example, swelling tests could focus on comparing solutions of differing ionic strengths and explore the charge screening effect and osmotic strength in greater detail. In addition to masses, the diameter and thickness of the hydrogels could be measured to determine volume. With respect to compression testing, institutions without Instron instruments could measure height deviations with incremental addition of weights to compress the gels.[40] Alternatively, students could be tasked with designing mechanical or physical property testing methods, such as slicing the gels, bending them, or adding imprints, for an exploratory-based experience. We found that the most challenging aspect of the experiment was evaluating the stress-strain data and calculation of modulus in the polymer course. We would recommend providing students with a pre-lab assignment that gave them practice doing so before analyzing their own data. In addition to/in place of comparison of the dried lactose methacrylate hydrogels to sodium polyacrylate from diapers, polysaccharide cellulose (cotton) or polyhydroxyethylmethacrylate (used in soft contact lens) could be studied. These are just a few examples of potential variations for adoption with this versatile hydrogel experiment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.XXXXXXX. [ACS will fill this in.] Instructor information for polymer laboratory (Version A) and organic chemistry laboratory (Version B), assignment handout (Version A and B), data from experiment development and course implementations, and Google form survey questions (PDF, DOCX)

AUTHOR INFORMATION

Corresponding Author

Jane E. Wissinger – Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United states; orcid.org/0000-0002-9240-3629; E-mail: jwiss@umn.edu

Authors

Jeffrey P. Buenaflor – Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United states; orcid.org/0000-0001-7823-0621

Marc A. Hillmyer – Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, United states; orcid.org/0000-0001-8255-3853

Michael T. Wentzel – Department of Chemistry, Augsburg University, Minneapolis, Minnesota 55455, United states; orcid.org/0000-0002-1148-2717

Notes

The authors declare no competing financial interests

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